Luminescent 2-(Hydroxyaryl)-1*H*-naphth[2,3-*d*]imidazole Derivatives

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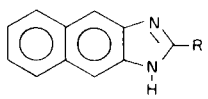
The synthesis and spectroscopic properties of a new class of luminescent 1*H*-naphth[2,3-*d*]-imidazole compounds are described. The ultraviolet spectra of 2-(hydroxyaryl)-1*H*-naphth[2,3-*d*]-imidazole derivatives are presented and discussed. Significant effects of structure and physical state of the luminescent compounds are observed on the measured emission wave length throughout the visible spectrum. The luminescence quantum efficiency of one of the naphthimidazole derivatives is reported.

The chemistry of the 1*H*-naphth[2,3-*d*]imidazole system has been relatively unexplored even though the parent compound was first synthesized as early as 1935 (1). Much of the interest in this class of heterocyclic compounds in the chemical literature to date has been in the synthesis of a limited number of simple derivatives (2,3). Most of these derivatives are representative examples of the 2-substituted 1*H*-naphth[2,3-*d*]imidazoles (**1**, R = alkyl, aryl, -OH, -SH, -NHR) (1,3,4). The 2-mercapto-1*H*-naphth[2,3-*d*]imidazole (**1**, R = -SH) is the only reported example of a luminescent compound in this heterocyclic class (3). We now describe the synthesis and luminescence properties of a new series of 2-(hydroxyaryl)-1*H*-naphth[2,3-*d*]imidazoles (**3** and **4**).



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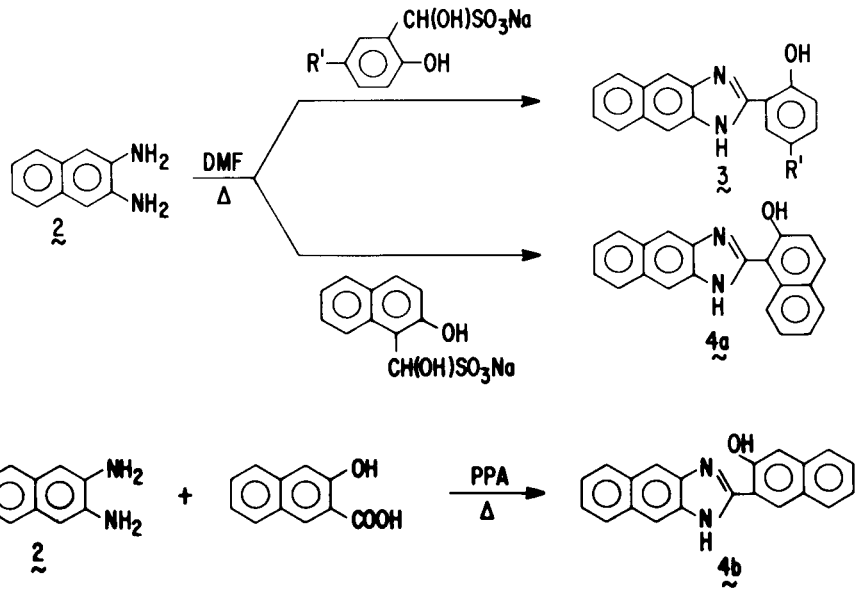
Results and Discussion

1. Synthesis.

The compounds **3** (R' = H, -OCH$_3$, -OH, C$_6$H$_5$) and **4a** were prepared according to a literature procedure (5) involving the thermal condensation of 2,3-diaminonaphthalene (**2**) with the bisulfite adduct of the corresponding aldehydes in dimethylformamide (Scheme I). The syn-

SCHEME I



thesis of **4b** involved the reaction of **2** with 3-hydroxy-2-naphthoic acid in polyphosphoric acid (6) (Scheme 1). Presumably either method could be used to prepare compounds **3** or **4** depending upon availability of aromatic aldehyde or carboxylic acid. The products were obtained in moderate yields and were high melting non-volatile solids. These compounds were sparingly soluble in most common organic solvents; however, a limited number displayed moderate solubility in methylene chloride and acetic acid. Preliminary observations indicate this class of compounds to be oxidatively and thermally stable (<250°).

II. Spectroscopic Properties. A. Ultraviolet Spectra.

The data available with respect to the ultraviolet absorption properties of the 1*H*-naphth[2,3-*d*]imidazole system is presently very limited. A study of the effect of *p*H on the absorption properties of several derivatives of this class of heterocyclics represents the only literature report on this subject (3). In an effort to more fully understand the luminescence properties of the 2-(hydroxyaryl)-1*H*-naphth[2,3-*d*]imidazoles, it was of interest to examine the ultraviolet spectra of the parent compound (**1**, R = H), the

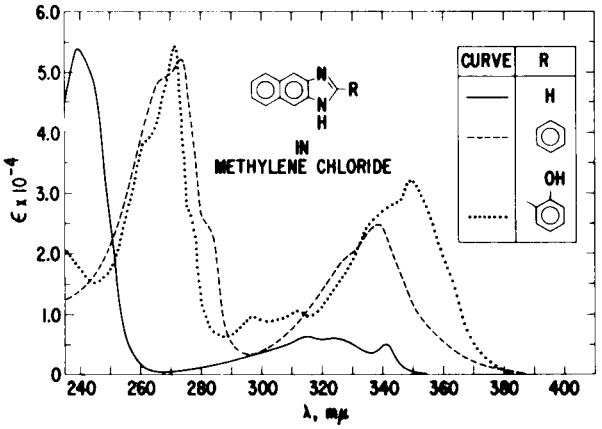


Figure 1

2-phenyl- (**1**, R = C_6H_5) and the 2-(2-hydroxyphenyl)- (3, R′ = H) derivatives (Figure 1). The absorption spectrum of **1** (R = H) possessed some similarity to the reported spectrum of 2-aminonaphthalene (7). Both spectra displayed broad band absorptions at 230-240 mμ ($\epsilon \sim 60{,}000$) and at 300-340 mμ ($\epsilon \sim 2000$-7000) characteristic of the transition of the substituted naphthalene chromophore. In analogy with related studies of the absorption properties of benzazoles (8), the basic chromophore in **1** (R = H) is considered to be the naphthalene ring and not the heterocyclic ring.

The spectra of the 2-aryl derivatives **1** (R = C_6H_5) and **3** (R′ = H) were similar but differed dramatically from the spectrum of the parent compound. The overall absorption band system of the aryl substituted compounds was considerably red-shifted relative to **1** (R = H), particularly in the short wavelength region. In addition to the bathochromic shift of the long wavelength bands, a significant increase in intensity of these bands was noted. This stronger and longer wavelength absorption can be ascribed to the introduction of a new benzylidene-imine chromophore in both **1** (R = C_6H_5) and **3** (R′ = H). The major difference between the absorption spectra of the two aryl 1*H*-naphth[2,3-*d*]imidazoles appeared in the long wavelength region. The effect of the *ortho*-hydroxyl group in **3** (R′ = H) was such as to cause a band separation presumably isolating the benzylidene-imine chromophore at 348 mμ from weak transitions of the naphthalene chromophore at ~300 mμ. Both of these transitions were present as one band system in **1** (R = C_6H_5) from 300-370 mμ. In spectral studies of 2-phenyl- and 2-(hydroxyphenyl)benzazoles (see Figure 2),

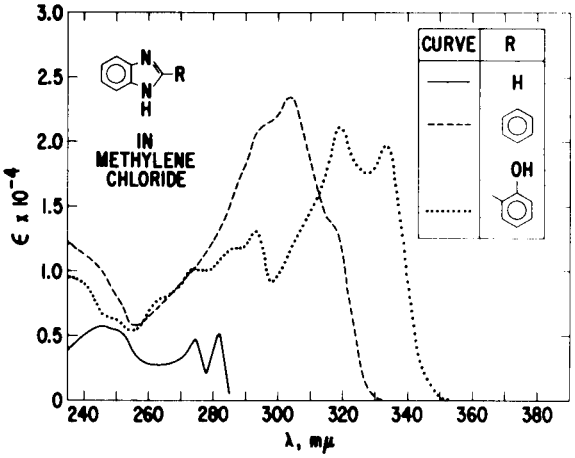


Figure 2

similar but more pronounced effects were observed (8). A spectral comparison of the 2-(hydroxynaphthyl)-1*H*-naphth[2,3-*d*]imidazoles **4a** and **4b** and the *ortho*-hydroxy

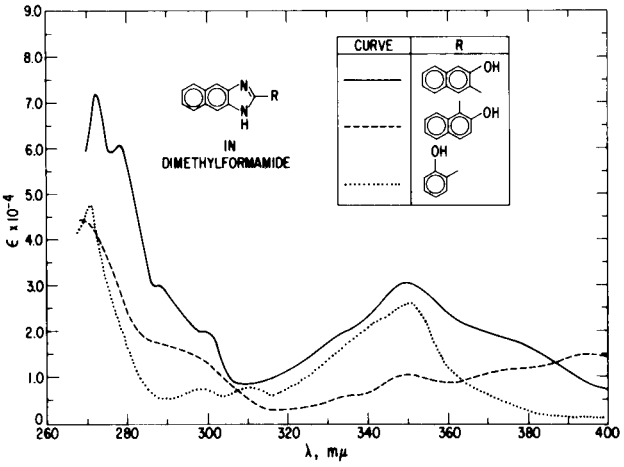


Figure 3

phenyl derivative **3** (R′ = H) indicated a basically similar absorption band system for the three compounds (Figure 3).

B. Luminescence Spectra.

The luminescence spectra of the 2-(hydroxyaryl)-1*H*-naphth[2,3-*d*]imidazole derivatives (**3** and **4**) in both methylene chloride solution and in the solid state displayed broad and essentially structureless emission bands. These data clearly demonstrate the dependence of luminescence wavelength on the structure of hydroxyaryl groups (see Table I).

TABLE I

Luminescence Spectral Data
(λ excit 250-400 mμ)

Compound	R′	λ^{solid}_{emiss} mμ	$\lambda^{CH_2Cl_2}_{emiss}$ mμ	Emission Band Width, mμ (a)
3	H	468	485	62
4a	-	485	465	62
3	C_6H_5	490	512	62
3	OH	515	530	65
3	OCH_3	520	545	72
4b	-	610	480	95

(a) Width at half height of emission band measured in methylene chloride.

The effect of these structural differences upon the emission properties in the solid state was such that luminescence throughout the visible region from blue (468 mμ) to red (610 mμ) was observed. A small but systematic bathochromic shift of the emission wavelength was apparent in the hydroxyaryl derivatives **3** as the R′ group was successively changed from hydrogen, phenyl, hydroxyl to methoxyl. This effect may be related to the electron donating ability of the respective R′ substituents (9). Subtle structural differences between the isomeric naphthimidazoles **4a** and **4b** resulted in an unusually large separation of the corresponding luminescence maxima (Δλ = 125 mμ). Although the emission band shape and wavelength maximum of a luminescent compound is very much dependent upon its physical state (10), the wavelength shift represented by the band maxima of compound **4b** in solution and in the solid state is unusually large (130 mμ). In addition, the emission band of **4b** in solution exhibits a comparatively broad band width (see Table I).

Definitive analysis of solution emission and absorption spectra for mirror symmetry was not possible since the emission bands were uncorrected. However, it was apparent from the observed solution absorption and emission data that the respective 0-0 bands did not overlap and significant Stokes shifts (11) were noted (Figure 4). This

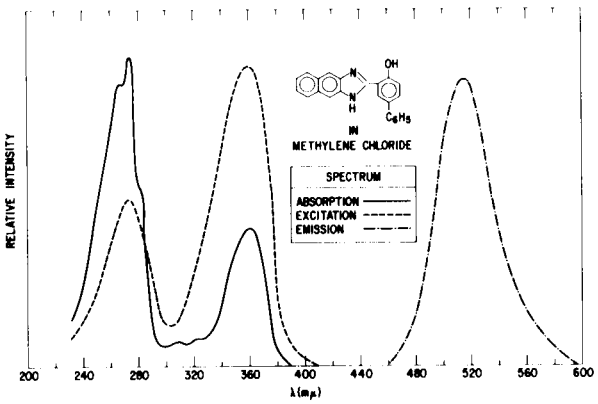


Figure 4

particular phenomenon was also observed in some recent spectroscopic studies of luminescent 2-(hydroxyphenyl)-benzazole derivatives (12). It is interesting to note that the excitation spectra of the 1*H*-naphth[2,3-*d*]imidazole derivatives were not identical to the corresponding absorption spectra. While the band maxima appeared at the same wavelength, the relative intensities of the band systems were reversed. The absorption, emission and excitation spectra of 2-(4-hydroxy-3-biphenylyl)-1*H*-naphth[2,3-*d*]-imidazole (**3**, R = C_6H_5) are illustrated in Figure 4 and are considered representative of this class of compounds. The luminescence quantum efficiency of the latter compound (**3**, R = C_6H_5) was found to be 0.50 relative to fluorescein as a standard (13).

The luminescence mechanism for the photochromic azomethine derivatives has been extensively investigated over the past several years (14). Comparable studies of the structurally analogous 2-(hydroxyphenyl)benzazoles and related systems have not been reported in the literature to date. The controversial mechanistic proposals for the luminescent azomethines clearly exclude any sound extrapolation from these studies to the heterocyclic systems (14b). Further investigation of the luminescence properties of this general class of heterocyclics is necessary for the elucidation of the emission mechanism.

EXPERIMENTAL

All melting points were determined on a Mel-Temp apparatus and are uncorrected. The ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. The luminescence spectra were recorded on an Aminco-Bowman spectrophotofluorometer equipped with a high pressure xenon lamp source and a 1P-128 detector.

Reagents.

The methylene chloride used in the luminescence measurements was redistilled reagent grade solvent. The 2,3-diaminonaphthalene, 2,5-dihydroxybenzaldehyde, 2-hydroxy-1-naphthaldehyde and 3-hydroxy-1-naphthoic acid were purchased from Aldrich Chemical

Company. Both 5-methoxysalicylaldehyde (oil) and 5-phenylsalicylaldehyde (m.p. 97-98°) were prepared by the method of Duff (15). 1*H*-Naphth[2,3-*d*]imidazole (m.p. 220°) was prepared according to the literature (1).

General Synthesis of 1*H*-Naphth[2,3-*d*]imidazole **3** and **4a**.

An equimolar mixture of 0.004 to 0.006 mole of the aldehyde sodium bisulfite adduct and 2,3-diaminonaphthalene in 25 to 50 ml. of DMF was heated at 150° for 14 hours. The reaction mixture was cooled, quenched with 50 ml. of water and the solid which precipitated was filtered and dried. Recrystallization from acetic acid and/or vacuum sublimation in a kugelrohr apparatus at 250-280°/0.1 mm gave analytically pure products.

2-(2-Hydroxyphenyl)-1*H*-naphth[2,3-*d*]imidazole (**3**, R′ = H).

Prepared according to the method described as light yellow crystals (51%), m.p. 340-346° dec. (recrystallized from acetic acid); λ max (methylene chloride), mμ (ε): 263 sh (39,677), 271 (54,190), 297 (8,300), 310 (10,100), 340 sh (27,200), 350 (31,900); λ emiss: 468 mμ (solid), 485 mμ (methylene chloride).

Anal. Calcd. for $C_{17}H_{12}N_2O$ (M.W. 260.29): C, 78.43; H, 4.64; N, 10.7. Found: C, 78.30; H, 4.70; N, 10.90.

2-(2-Hydroxy-1-naphthyl)-1*H*-naphth[2,3-*d*]imidazole (**4a**).

Prepared according to the method described as soft yellow needles (28%), m.p. 337-339° dec. (sublimed and recrystallized from acetic acid); λ max (methylene chloride), mμ (ε): 255 (42,400), 287 (13,950), 297 sh (12,600), 313 (8,900), 327 (15,900), 370 (25,700); λ emiss: 485 mμ (solid), 465 mμ (methylene chloride).

Anal. Calcd. for $C_{21}H_{14}N_2O$ (M.W. 310.34): C, 81.27; H, 4.54; N, 9.02. Found: C, 80.80; H, 4.60; N, 9.04.

2-(4-Hydroxy-3-biphenylyl)-1*H*-naphth[2,3-*d*]imidazole (**3**, R′ = C_6H_5).

Prepared according to the method described as yellow crystals (13%), m.p. 328-330° dec. (sublimed); λ max (methylene chloride), mμ (ε): 263 (65,200), 273 (74,000), 280 sh (40,700), 308 sh (7,900), 325 sh (12,700), 355 (28,000); λ emiss: 490 mμ (solid), 512 mμ (CH_2Cl_2).

Anal. Calcd. for $C_{23}H_{16}N_2O$ (M.W. 336.38): C, 82.11; H, 4.79; N, 8.32. Found: C, 82.20; H, 4.80; N, 8.31.

2-(2,5-Dihydroxyphenyl)-1*H*-naphth[2,3-*d*]imidazole (**3**, R′ = OH).

Prepared according to the method described as tan crystals (33%), m.p. >380° (sublimed and recrystallized-acetic acid); λ max (95% ethanol) (16), mμ (ε): 262 (40,200), 272 (55,200), 278 sh (19,300), 324 (12,900), 356 (23,900), 370 (19,400); λ emiss: 515 mμ (solid), 530 mμ (methylene chloride).

Anal. Calcd. for $C_{17}H_{12}N_2O_2$ (M.W. 276.29): C, 73.89; H, 4.38; N, 10.1. Found: C, 73.40; H, 4.33; N, 9.81.

2-(2-Hydroxy-5-methoxyphenyl)-1*H*-naphth[2,3-*d*]imidazole (**3** R′ = OCH_3).

Prepared according to the method described as yellow needles (54%), m.p. 338-342°, dec. (sublimed); λ max (95% ethanol) (16), mμ (ε): 273 (53,900), 280 sh (24,700), 310 (7,200), 323 (11,100), 359 (26,100), 370 (23,500); λ emiss: 520 mμ (solid), 545 mμ (methylene chloride).

Anal. Calcd. for $C_{18}H_{14}N_2O_2$ (M.W. 290.31): C, 74.46; H, 4.86; N, 9.65. Found: C, 74.09; H, 4.78; N, 9.70.

Preparation of 2-(3-Hydroxy-2-naphthyl)-1*H*-naphth[2,3-*d*]imidazole. (**4b**) Using PPA Method.

A solution of 1.58 g. (0.01 mole) of 2,3-diaminonaphthalene and 1.88 g. (0.01 mole) of 3-hydroxy-2-naphthoic acid in 60 g. of PPA was heated at 200° for 24 hours. The cooled reaction mixture was quenched with an equal volume of water and neutralized with solid sodium hydroxide. The solid which precipitated was filtered and vacuum sublimed at 340°/0.1 mm in a kugelrohr apparatus to give yellow-green crystals of the naphthimidazole, 0.362 g. (12%), m.p. 340-342°, dec.; λ max (DMF) (16), mμ (ε): 272 (71,900), 278 (60,700), 289 sh (30,100), 300 sh (20,400), 335 (30,400), 349 (31,100), 375 (18,400); λ emiss: 610 mμ (solid), 480 mμ (methylene cholride).

Anal. Calcd. for $C_{21}H_{14}N_2O$ (M.W. 310.34): C, 81.26; H, 4.54; N, 9.02. Found: C, 81.60; H, 4.6; N, 8.92.

Preparation of 2-Phenyl-1*H*-naphth[2,3-*d*]imidazole.

A solution of 0.415 g. (0.0026 mole) of 2,3-diaminonaphthalene and 0.44 g. (0.0026 mole) of benzaldehyde sodium bisulfite adduct in 35 ml. DMF was heated 14 hours at 150°. Quenching the reaction mixture with water and extraction with ethyl acetate gave the naphthimidazole, 0.10 g. (14%), m.p. 215-217°; λ max (95% ethanol), mμ (ε): 264 (34,500), 273 (36,000), 327 sh (13,000), 338 (17,000).

Anal. Calcd. for $C_{17}H_{12}N_2$ (M.W. 244.29): C, 83.57; H, 4.95; N, 11.43. Found: C, 83.30; H, 4.94; N, 11.16.

REFERENCES

(1) K. Fries, R. Walter, and K. Schilling, *Ann. Chem.*, 516, 248 (1935).

(2) D. J. Brown, in "Current Trends in Heterocyclic Chemistry," A. Albert, G. M. Badger and C. W. Shoppee, Eds., Academic Press, Inc., New York, N. Y., 1958, p. 75.

(3) D. J. Brown, *J. Chem. Soc.*, 1974 (1958).

(4a) H. Goldstein and M. Streuli, *Helv. Chim. Acta*, **20**, 520 (1937); (b) W. Ried and E. Torinus, *Chem. Ber.*, **92**, 2902 (1959). (c) B. L. Bastic, V. B. Golubovic, *Glasnik Khem. Drushtva Beograd*, **18**, 235 (1953); *Chem. Abstr.*, **52**, 2005g (1958); (d) Kalle A-G British Patent, 895,001; *Chem. Abstr.*, **57**, P14578e (1962); (e) Ciba Ltd., Belgian Patent, 620,372; *Chem. Abstr.*, **59**, P14146b (1963); (f) Kalle A-G, German Patent, 1,137,625; *Chem. Abstr.*, **59**, 11515b (1963); (g) G. R. Revankai, S. Siddappa and D. C. Umarani, *Indian J. Chem.*, **2**, 489 (1964); *Chem. Abstr.*, **62**, 10429f (1965).

(5a) D. Jerchel, H. Fisher and M. Krocht, *Ann. Chem.*, 575, 162 (1952); (b) H. F. Ridley, R. G. W. Spickett and G. M. Timmis, *J. Heterocyclic Chem.*, **2**, 453 (1965).

(6) D. W. Hein, R. J. Alheim and J. J. Leavitt, *J. Am. Chem. Soc.*, **79**, 427 (1957); U. S. Patent, 2,985,661.

(7) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 304.

(8a) R. Passerini, *J. Chem. Soc.*, 2256 (1954); (b) A. Cerniani and R. Passerini, *ibid.*, 2261 (1954).

(9a) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 256-259. (b) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Wiley Interscience, 1969, pp. 139-141.

(10) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p. 281.

(11) Stokes shift may be defined as the wavelength or energy difference between the corresponding 0-0 bands of absorption and luminescence.

(12) J. G. Wirth, C. M. Orlando, Jr. and D. R. Heath, "Structural Effects on the Luminescence Properties of 2-(2-Hydroxyphenyl)-benzazoles," publication in preparation.

(13) W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, 72, 3251 (1968).

(14a) O. A. Osipov, Y. A. Zhdanov, M. I. Knyazhanskii, V. I. Minkin, A. D. Garnovskii and I. D. Sadekov, *Russ. J. of Phys. Chem.*, 41, 322 (1967); (b) W. F. Richey and R. S. Becker, *J. Chem. Phys.*, 49, 2092 (1968).

(15) J. C. Duff, *J. Chem. Soc.*, 547 (1941).

(16) The ultraviolet spectra of these compounds were also measured in methylene chloride, but due to problems of insolubility, only the positions of the absorption maxima and not the corresponding extinction coefficients were obtained in this solvent. The absorption spectra of compounds **3** (R′ = OH) and **3** (R′ = OCH_3) in 95% ethanol and of **4b** in DMF were very similar to the corresponding spectra taken in methylene chloride except for the position of the longest wavelength maxima; λ max (methylene chloride), **3** (R′ = OH), 357 mμ; **3** (R′ = OCH_3), 360 mμ; **4b**, 348 mμ.

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